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RESEARCH PROJECT INITIATION

Date: June 11, 1974

Project Title: Research Initiation - Transport Phenomena in Liquid Metals.

Project No: E-19-624

Principal Investigator: Dr. Anthony L. Hines

Sponsor: National Science Foundation

Agreement Period: From April 1, 1974 Until March 31, 1976*
*13 month budget period plus 5 months for submission of required reports, etc.

Type Agreement: Grant GK-42086

Amount: $17,000 - NSF Funds (E-19-624)
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Reports Required: Annual Letter Technical; Final Report

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RA-3 (6-71)

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SPONSORED PROJECT TERMINATION

Date: August 19, 1976

Project Title: Transport Phenomena in Liquid Metals

Project No: E-19-624

Project Director: Dr. A. L. Hines

Sponsor: National Science Foundation

Effective Termination Date: 3/31/76

Clearance of Accounting Charges: all clear

Grant/Contract Closeout Actions Remaining: NONE

- _ Final Invoice and Closing Documents
- _ Final Fiscal Report
- _ Final Report of Inventions
- _ Govt. Property Inventory & Related Certificate
- _ Classified Material Certificate
- _ Other _____

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CA–4 (3/76)

ANNUAL TECHNICAL LETTER

Georgia Institute of Technology

Principal Investigator:	Anthony L. Hines
Grant Number:	GK 42086
Starting Date:	April 1, 1974
Completion Date:	March 31, 1976
Grant Title:	Transport Phenomena in Liquid Metals

Research and Results

The primary objective of this research is to study diffusion in liquid metals both theoretically and experimentally by the shear cell method. During the past year, the experimental apparatus has been fabricated, assembled and tested. Diffusion coefficients are presently being measured for the binary system mercury-zinc diffusing into the same alloy. A modified shear cell has been developed to measure the diffusion coefficients of metals with high melting points. It will be tested by measuring diffusion coefficients for thallium at high temperatures. Because of insufficient experimental data, reporting of diffusion coefficient will be delayed until the final report is written.

A theoretical diffusion equation has been developed along the lines of a modified small fluctuation theory. It has proven to be successful for predicting self-diffusion coefficients.

The Scientific collaborators involved in the research are David D. Arnold and John E. Popielarczyk. Both are candidates for the Master of Chemical Engineering degree and they will each write a thesis dealing with liquid metal diffusion.

The experimental data of Runs 1 and 14 of Campbell and Hills[3] were used. Unfortunately, the D_e-value and the pellet size were not written, though it was mentioned that the experimental techniques were the same as those employed in their previous work.[4] Assuming that the shrinkage of the pellet does not occur during the reaction, the porosity of the oxide shell, ϵ^{CaO}, was calculated to be 0.69 for Run 1, and the effective diffusivity, D_e, at $\epsilon^{CaO} = 0.69$ was estimated[3] to be 0.219 cm^2/s. The pellet diam was assumed[4] to be 1.1 cm. The temperature at the reaction interface, T_i, was reported to be between 820° and 830°C. Then the rate constant, k_c, calculated from Eq. [2] was between 1.73×10^{-3} and 2.95×10^{-3} g $CaCO_3/cm^2 \cdot s \cdot atm$ at different r^* values. No systematic variations were observed, and the mean value was 2.36×10^{-3}. Similarly, the mean k_c-value for Run 14 was 4.04×10^{-3}.

On the other hand, Philbrook and Natesan[5] developed a rate equation in which the processes of mass transfer and interfacial reaction are involved, and they estimated the rate constant, k_{ls}, by fitting the calculated fractional reaction to the experimental data of Furnas.[6] This rate constant is correlated with k_c in Eq. [2] as

$$k_c = \frac{M}{p^e_{CO_2}} k_{ls} \exp\left(-\frac{\Delta H^{\ddagger} + RT_{av}}{RT_i}\right) \qquad [3]$$

In our fluidization experiment carried out at 850°C, the temperature at the interface was estimated to be about 825°C.[1] The rate constant, k_c, at this temperature was calculated from Eq. [3] to be 2.7×10^{-3} which is very close to the value estimated above. The k_c-value employed in our limestone paper[1], 3.08×10^{-4} g $CaCO_3/cm^2 \cdot s \cdot atm$, is about one tenth of the values estimated here.

By using the k_c-value of 2.36×10^{-3}, the results of our Exp. Nos. 6 and 15 were re-examined. In Exp. No. 6, an excellent coincidence was obtained between the observed and calculated fractional decompositions despite of the large increase in the k_c-value. This indicates that the resistance of interfacial reaction is minor. In Exp. No. 15, on the other hand, the difference between the observed and calculated fractional reactions was fairly large when this k_c-value was employed. In order to superimpose the calculated and experimental fractional reactions with each other, the heat transfer coefficient, h_w, of 90.0 $kcal/m^2 \cdot h \cdot °C$ should be employed instead of 352.8 $kcal/m^2 \cdot h \cdot °C$.[1] This value of 90.0 $kcal/m^2 \cdot h \cdot °C$ seems not to be unreasonably low, though the calculated particle temperature was about 60°C lower than the observed temperature. The fractional resistances of interfacial reaction, diffusion of CO_2 through the oxide shell and mass transfer through the gas boundary film, η_1, η_2 and η_3, respectively, were calculated, and they are listed in Table I. As seen in this table, η_1 is still much higher than η_2 and η_3. Thus it can be said that the overall rate of reaction is mainly controlled by the rates of interfacial reaction and the heat transfer from reactor wall to fluidized bed. This is again on the same line as the result described in our paper.[1]

Table I. Fraction of Resistances

Experiment	Fractional Decomposition	η_1	η_2	η_3
Fluidized Bed	0	0.979	0	0.021
Exp. No. 15	0.2	0.947	0.037	0.016
	0.4	0.917	0.070	0.013
	0.6	0.889	0.102	0.009
	0.8	0.870	0.124	0.006
Campbell and Hills[3]	0	0.613	0	0.387
Run 1	0.2	0.534	0.192	0.274
	0.4	0.471	0.331	0.198
	0.6	0.422	0.444	0.134
	0.8	0.398	0.517	0.085

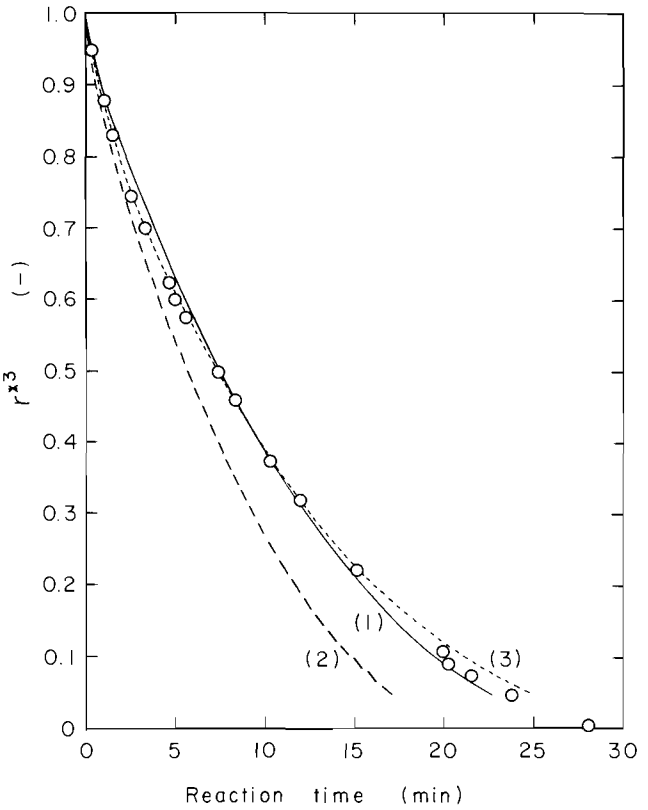

Fig. 1—r^{*3} *vs* reaction time: Curve 1: $D_e = 0.219$, $k_e = 1.035 \times 10^{-3}$, $k_C = 2.36 \times 10^{-3}$ Curve 2: $D_e = 0.219$, $k_e = 1.035 \times 10^{-3}$; Curve 3: $D_e = 0.078$, $k_e = 2.054 \times 10^{-3}$.

In order to further investigate the k_c-value, it was tried to calculate the overall rate of thermal decomposition of a single spherical pellet under the conditions of Run 1 of Campbell and Hills.[3] The effective diffusivity of CO_2 gas, D_e, and the effective thermal conductivity, k_e, in the oxide shell were assumed to be 0.219 cm^2/s and 1.035×10^{-3} $cal/cm \cdot s \cdot °C$, respectively. The k_c-value of 2.36×10^{-3} was used. Eq. [2] and the following rate equation of heat transfer:

$$\frac{4\pi r_o^2 (T_G - T_i)}{\frac{1}{h_T} + \frac{r_o}{k_e r^*}(1 - r^*)} - \dot{n}\Delta H = m_{th}\frac{dT_i}{d\theta} \qquad [4]$$

were solved simultaneously. The calculated r^{*3} shown with solid line (curve 1) in Fig. 1 coincided with observed value. The calculated fractional resistances, η_1, η_2 and η_3, are also listed in Table 1: both resistances of η_1 and η_2 are in the same magnitude.

Furthermore, a calculation was made to estimate the overall rate of reaction by omitting the $(1/RT_i k_c)$-term in Eq. [2]. This means that the reaction is re-

garded to be mass transfer and diffusion control. Curve 2 in Fig. 1 represents the calculated r^{*3}, which is far lower than the observed value. It was also tried to fit the calculated curve to the experimental data by adjusting the ϵ_{CaO}-value, thus changing D_e and k_e at the same time, and a pair of $D_e = 0.078$ and $k_e = 2.05 \times 10^{-3}$ was obtained[3] at $\epsilon_{CaO} = 0.475$. The fitted curve (3) is illustrated in Fig. 1. However, this ϵ_{CaO}-value of 0.475 corresponds to the shrinkage of about 40 pct in volume. It was also found that the calculated temperature at the reaction interface is about 40°C higher than the observed temperature at the later stages of decomposition. This result is different from the calculation made by Campbell and Hills. Probably their numerical values of D_e and k_e were different.

Though there still remains a few uncertainties in estimating the k_c-value, it is thought that the true value is between 10^{-3} and 10^{-2}.

Nomenclatures

c_i : CO_2 concentration at reaction interface, mole/cm^3
c_e : equilibrium CO_2 concentration, mole/cm^3
c_o : bulk CO_2 concentration, mole/cm^3
D_e : effective diffusivity of CO_2 through oxide shell, cm^2/s
h_T : total heat transfer coefficient, cal/(cm^2)(s)(°C)
k_c : rate constant of interfacial reaction, g $CaCO_3$/(cm^2)(s)(atm)
k_e : effective thermal conductivity of oxide shell, cal/(cm)(s)(°C)
k_g : film coefficient of mass transfer, cm/s
M : molecular weight of $CaCO_3$, g/mole
m_{th} : thermal mass, cal/°C
$\dot{n}$: rate of reaction, mole/s
$p^e_{CO_2}$: equilibrium partial pressure of CO_2, atm
r_i : radius of reaction interface, cm
r_o : particle radius, cm
r^* : $= r_i / r_o$
T_G : gas temperature, K
T_i : temperature at reaction interface, K
w : weight of limestone, g
ϵ_{CaO} : porosity of decomposed oxide shell
θ : time, s
ρ : density, g/cm^3

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A Small Fluctuation Theory for Diffusion in Liquids

ANTHONY L. HINES, HUGH A. WALLS, AND DAVID W. ARNOLD

Swalin's[1] small fluctuation theory is developed from a model of the liquid state in which local density fluctuations and the cooperative movements of atom clusters give rise to diffusion. Although the model predicts accurately diffusion coefficients for mercury, cadmium and tin, agreement with experimental data for other liquids is poor. It is demonstrated herein that this is at least partially the consequence of Swalin's definition of available diffusion paths and his assumption that energy fluctuations result from the elongation of four nearest neighbor bonds.

Following the treatments of Einstein,[2] Furth,[3] and Swalin,[1] the probability of finding an atom fluctuating in the range from j to $j + dj$ is:

$$p(j)dj = cj^2 \exp[-E(j)/kT]dj \quad [1]$$

where c is a constant, j is the displacement distance, and $E(j)$ is the energy associated with the fluctuation.

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Since all atoms experience movements and tend to diffuse away from their neighbors, the total probability is equal to one and the constant is:

$$c = \left[\int_0^\infty j^2 \exp[-E(j)/kT]dj\right]^{-1} \quad [2]$$

Furthermore, the mean square fluctuation distance is:

$$\bar{j}^2 = \int_0^\infty j^2 p(j)dj \quad [3]$$

which, when combined with Eq. [1], gives:

$$\bar{j}^2 = \frac{\int_0^\infty j^4 \exp[-E(j)/kT]dj}{\int_0^\infty j^2 \exp[-E(j)/kT]dj} \quad [4]$$

The Morse function, which Swalin assumed to be suitable for predicting binding energies between molecular pairs in liquids, is:

$$\epsilon = \epsilon_D[1 + \exp(-2\alpha j) - 2\exp(-\alpha j)] \quad [5]$$

where ϵ_D is the dissociation energy of an atomic bond and α is related to the curvature of the potential vs distance curve. From quasi-chemical theory, ϵ_D may be estimated as:

$$\epsilon_D = \frac{2\Delta H_v}{ZN_0} \quad [6]$$

where Z is the number of near neighbors, N_0 is Avogadro's number and ΔH_v is the heat of vaporization. Since the removal of an atom from a cluster requires that $Z/2$ coordination bonds be broken, the fluctuation energy is given as $E(j) = (Z/2)\epsilon$. Therefore, the en-

ergy necessary to produce a fluctuation corresponding to the distance j is:

$$E(j) = \frac{\Delta H_v}{N_0}[1 + \exp(-2\alpha j) - 2\exp(-\alpha j)] \quad [7]$$

Eq. [7] is expanded in a Maclaurin's series, with all terms higher than second order neglected, and substituted into Eq. [4] and integrated to give:

$$j^2 = \frac{3N_0 kT}{2\Delta H_v \alpha^2} = \frac{6kT}{ZK} \quad [8]$$

where:

$$\alpha^2 = \frac{ZN_0 K}{4\Delta H_v} \quad [9]$$

and K is the Waser-Pauling[4] force constant.

From the absolute reaction rate theory, the vibrational frequency is expressed by the equation:

$$\nu = p\left(\frac{kT}{\hbar}\right)\left(\frac{F^*}{F}\right) \quad [10]$$

where p is the number of available diffusion paths, $\hbar$ is Planck's constant, and F^*/F is the ratio of the activated state partition function to the normal state partition function. Since F^*/F is about one:

$$\nu = p\frac{kT}{\hbar} \quad [11]$$

Although the maximum number of nearest neighbors possible with equally sized spheres is 12, the Z in the liquid state is somewhat less, usually closer to 8. This gives $12-Z$ available diffusion paths and results in a vibrational frequency of:

$$\nu = (12 - Z)kT/\hbar \quad [12]$$

Substituting Eqs. [8] and [12] into the Einstein equation ($D = \bar{j}^2\nu/6$) yields:

$$D = \frac{k^2T^2N_0(12-Z)}{4\hbar\Delta H_v\alpha^2} = \frac{k^2}{\hbar}\left(\frac{12-Z}{Z}\right)\frac{T^2}{K} \quad [13]$$

Swalin's derivation of the equation corresponding to Eq. [13] gave the following expression for the diffusion coefficient;

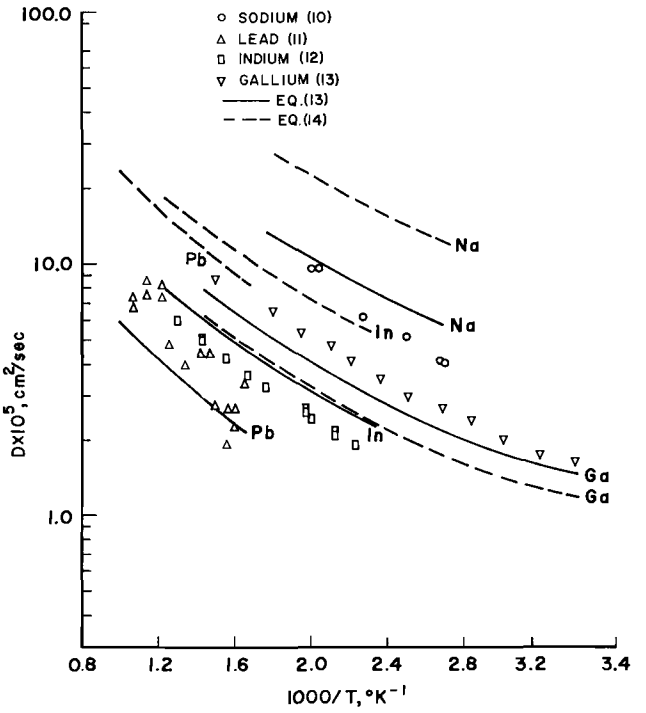

Fig. 2—Comparison of theory with liquid metals self diffusion coefficients.

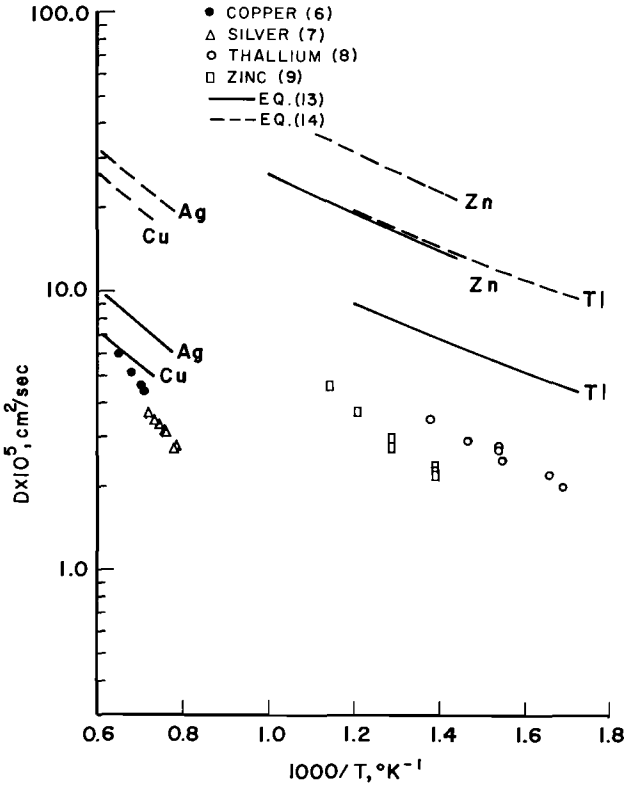

Fig. 1—Comparison of theory with liquid metals self diffusion coefficients.

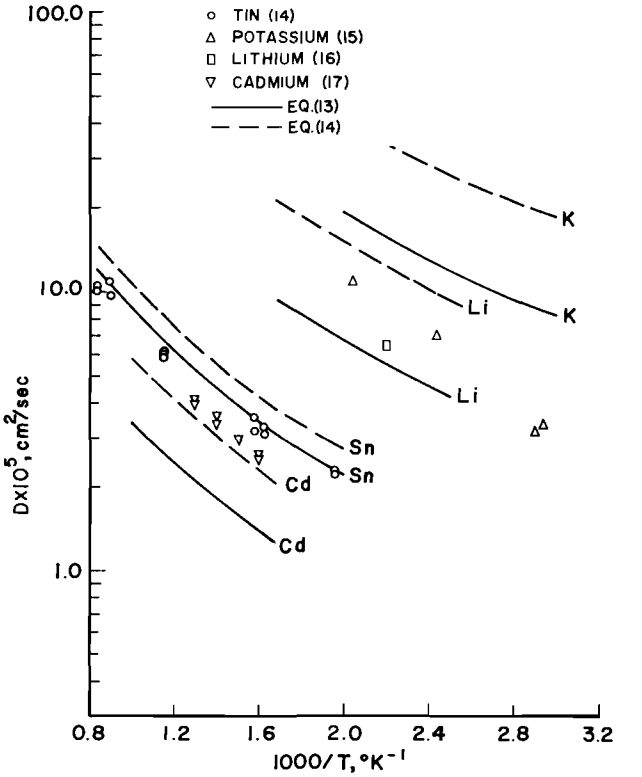

Fig. 3—Comparison of theory with liquid metals self diffusion coefficients.

$$D = \frac{3Z^2 N_0 k^2 T^2}{96\hbar\Delta H_v \alpha^2} = \frac{k^2 Z T^2}{8\hbar K} \qquad [14]$$

There are two principal differences in the derivations of Eqs. [13] and [14], viz., in Eq. [13] the number of available diffusion paths is $(12 - Z)$ and $Z/2$ coordination bonds must be broken for a fluctuation to occur, whereas in Eq. [14] Z diffusion paths are available and only 4 coordination bonds must be broken. The definition of Z suggests, however, that it cannot be the number of paths available.

Predictions of diffusion coefficients from Eqs. [13] and [14] are compared to self-diffusion data for thirteen liquid metal elements in Figs. 1 through 4. These comparisons show clearly the improved predictions given by Eq. [13] over those from Swalin's original equation for virtually all elements.

The coordination numbers used in Eq. [13] are shown in Table I. These values were calculated by Walls, Broome, and Hines[5] from the empty volume fraction at the melting point. It has been noted that the coordination number changes slowly with increasing temperature over a wide temperature range.[5] However, because the diffusion data considered here involve limited temperature ranges, generally not too far above the melting point, serious error is not introduced by using the coordination numbers determined at the melting point shown in Table I. Values of the Waser Pauling force constants used in our calculations are also given in Table I.

In contrast to the mean square fluctuation distance calculated by Swalin, the mean square fluctuation distance as represented by Eq. [8] is dependent upon the coordination number. This should be expected since the coordination number is related to both the amplitude and width of the first peak in the radial distribution function. Since the potential of the mean force curve is directly related to the *RDF* curve, the dependence of the mean square fluctuation distance on the coordination number is to be expected.

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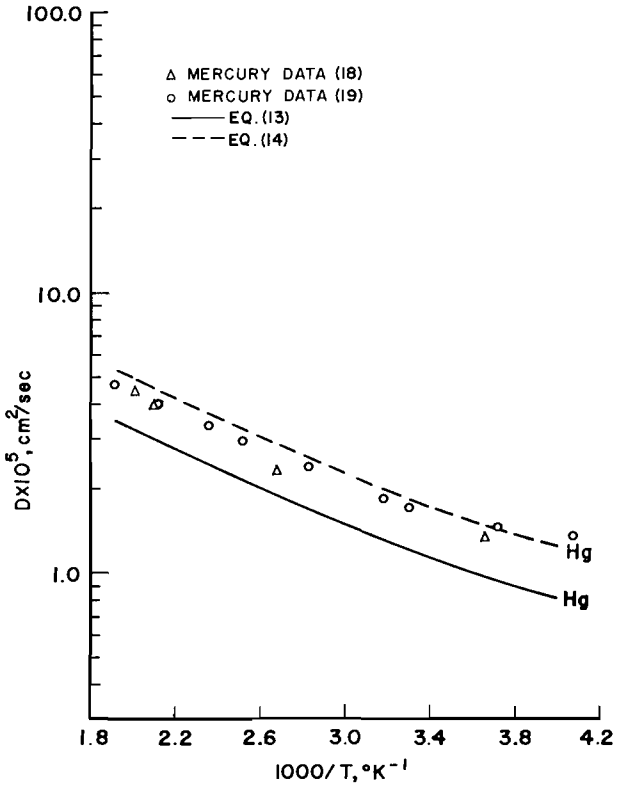

Fig. 4—Comparison of theory with liquid metals self diffusion coefficients.

Table I. Coordination Number at the Melting Point

Element	Z	K*	Element	Z	K*
Li	7.7	5.94	Ga	4.7	28.285
Na	7.6	4.05	Pb	9.1	15.31
K	7.7	2.201	In	7.8	12.526
Sn	6.0	33.13	Tl	7.6	12.8
Zn	6.8	7.975	Cu	9.0	36.9
Hg	6.6	18.0263	Ag	8.7	30.4
Cd	6.9	61.4			

*Expressed as (newton/meters) × 10^{-6}.

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Chlorination of Bauxite in the Presence of Silicon Tetrachloride

D. J. MILNE

The production of aluminum metal by electrolysis of chloride salt melts promises significant cost savings over the conventional Hall process. Currently a 15,000 tpy semi-commercial plant is undergoing trials in the United States.[1] The recently announced Toth process[2] also produces aluminum chloride

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FINAL TECHNICAL LETTER

Georgia Institute of Technology

Principal Investigator:	Anthony L. Hines
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Starting Date:	April 1, 1974
Completion Date:	March 31, 1976
Grant Title:	Transport Phenomena in Liquid Metals

SUMMARY

The purpose of this research program was to study diffusion in liquid metals both theoretically and experimentally. Diffusion coefficients were measured on the binary system, mercury-zinc diffusing into the same alloy, using a modified shear cell technique. Diffusion coefficients on the mercury-thallium alloy were also measured by the above method. The experimentally measured diffusion coefficients were compared with values measured by other methods and were found to be consistently higher for both the mercury-zinc and mercury-thallium amalgams. Experimentally determined diffusion coefficients, however, were compared with values calculated from various diffusion models and were found to be in reasonable agreement.

A theoretical diffusion equation was developed along the lines of a small fluctuation theory as developed by Swalin. It has been used to accurately predict self-diffusion coefficients over an extended temperature range.

RESEARCH AND RESULTS

Mercury-Thallium

The self-diffusion coefficients for 1.440 weight % thallium amalgams were measured by the modified shear-cell technique designed by Broome and Walls (1). The measurements were made at atmospheric pressure over the temperature range, $303^{o}K$ to $429^{o}K$, and are presented in Table 1. The solution to Fick's second law for the finite capillary geometry of the modified shear-cell, was used in a computer program to calculate self-diffussion coefficients.

To compare these results with other works, the self-diffusion coefficients were fitted to the Arrhenius type equation giving:

$$D = (5.58 \times 10^{-4}) \exp\left(\frac{1961.19}{RT}\right)$$

where:

D = self-diffusion coefficient, cm^2/sec

R = gas constant, (1.98717), cal/mole-^{o}K)

T = temperature, ^{o}K

The values of the activation energy and the pre-exponential factor in this work are compared to values from other works in Table 2. The values for the pre-exponential factor for the thallium amalgam were more than twice the value for pure thallium as shown by Barras et al.(2) and five to six times the pre-exponential factor for pure mercury. The activation energy for the thallium amalgam fell approximately half-way between Barras,et al's. value for pure thallium and the values for pure mercury. In Figure 1 the experimental data of this work is compared to the self-diffusion coefficients predicted from the Walls-Upthegrove (6) equation. The required density and viscosity data for the thallium amalgams were obtained from a paper by Foley,

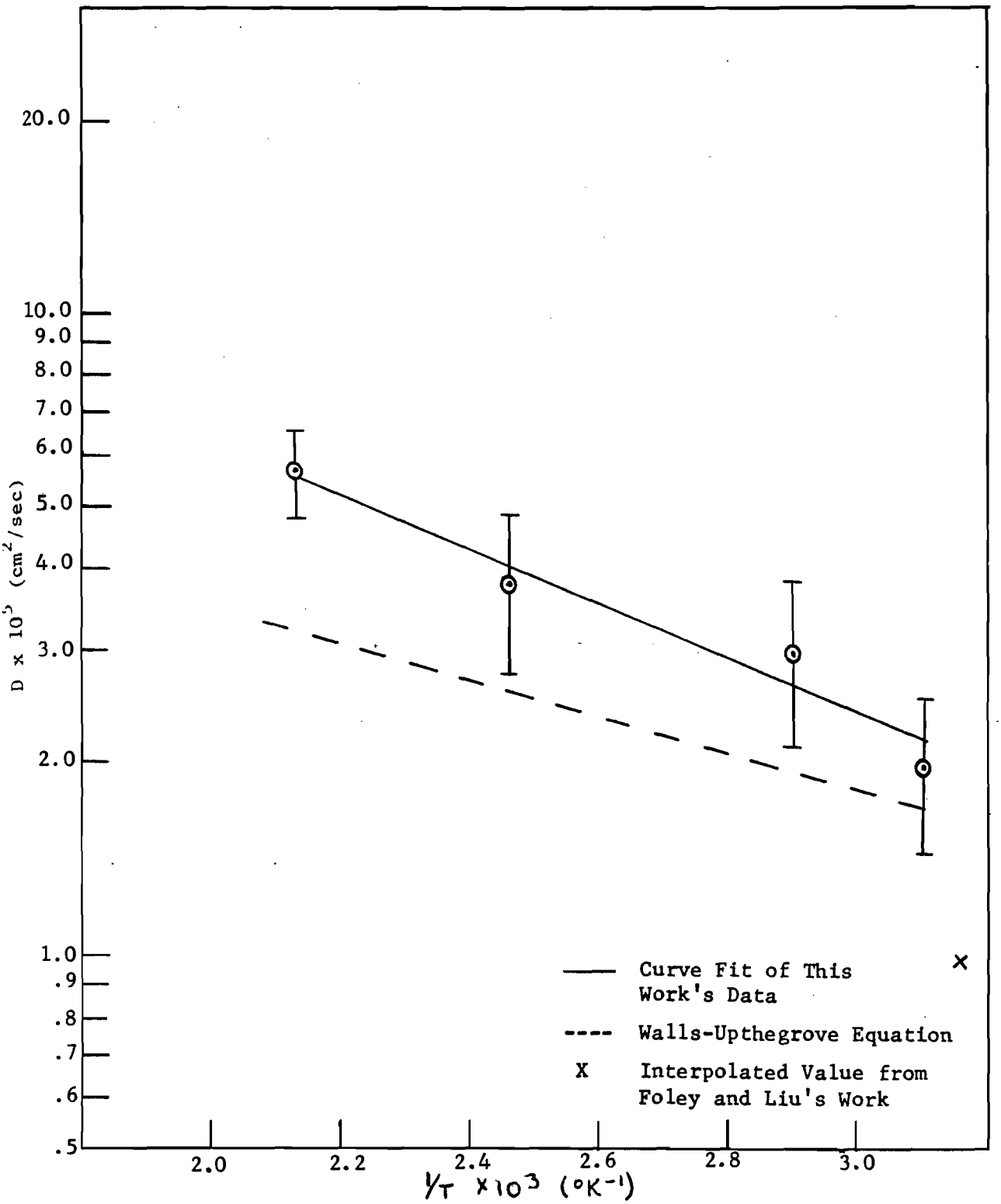

Figure 1. Self-Diffusion Data in 1.440 Weight Percent Thallium Amalgams

Table 1. Measured Self-Diffusion Coefficients in Thallium Amalgams at 1.440 Weight Percent Thallium

Temp ^{o}K	$D \times 10^{5}$ (cm^2/sec)	Time (sec.)	$\pm\Delta D \times 10^{5}$ (cm^2/sec)
305.7	1.4895	36469.	.03
303.2	1.2056	36803.	.03
303.2	2.3388	32396.	.03
303.2	1.5564	41999.	.02
303.2	1.7196	31747.	.03
303.2	1.0959	29898.	.03
303.2	2.3846	26047.	.04
322.7	1.9693	33780.	.15
322.7	2.8087	30840.	.19
322.7	2.1066	27300.	.18
322.7	4.4044	28380.	.23
322.7	3.7564	29580.	.21
322.7	1.3060	26705.	.15
322.7	3.9242	32531.	.21
322.7	3.3760	28380.	.22
322.7	3.0299	24826.	.03
322.7	2.8000	31565.	.04
322.7	1.4519	33538.	.03
322.7	3.5324	35944.	.04
322.7	3.2052	37085.	.04
322.7	2.7543	31429.	.04
322.7	3.3718	30972.	.04

Table 1. (Continued)

Temp °K	D x 10^5 (cm^2/sec)	Time (sec.)	+Δ D x 10^5 (cm^2/sec)
322.7	3.7666	32445.	.04
375.7	3.1761	27743.	.04
375.7	4.1149	31926.	.04
375.7	2.6137	48794.	.03
375.7	4.6185	24489.	.05
375.7	2.8593	25502.	.04
375.7	3.3040	34804.	.04
375.7	2.7918	31500.	.04
375.7	4.0879	25234.	.05
375.7	2.9534	32100.	.04
375.7	4.5415	33839.	.04
375.7	4.9379	30000.	.05
375.7	6.3087	33454.	.04
375.7	3.8544	30016.	.04
375.7	2.7792	33175.	.04
375.7	5.6074	33303.	.05
378.7	3.0822	28044.	.04
375.7	2.8719	25292.	.04
419.2	5.2485	34978.	.04
429.2	6.9154	34978.	.05
429.2	4.5664	32756.	.05
429.2	6.7695	25800.	.06
429.2	6.4530	27794.	.05

Table 1. (Continued)

Temp ^{o}K	$D \times 10^5$ (cm^2/sec)	Time (sec)	$+\Delta_2 D \times 10^5$ (cm^2/sec)
429.2	5.6793	28886.	.05
429.2	4.6758	29727.	.05
399.2	6.1456	28886.	.05
429.2	4.6313	42515.	.04

Table 2. Experimental Self-Diffusion Constants for the Arrhenius Equation for Liquid Metal Systems

System	Concentration	Do (cm^2/sec)	E (cal/mole)	Temperature Range (^oK)	Reference
Hg-T^l	1.414 At % T^l	5.58×10^{-4}	1961.2	303-429	This Work
T^l	Elemental	2.21×10^{-4}	2867	590-724	2
Hg	Elemental	1.26×10^{-4}	1160	-	3
Hg	Elemental	1.10×10^{-4}	1150	296-333	4
Hg	Elemental	$.85 \times 10^{-4}$	1005	273-371	5

Basak, and Delorey (7). The parameters b and γ were presented by Walls (8). The entropy of activation, $\Delta S^* = -1.54$ cal/mole ^oK, and the enthalpy of activation, $\Delta H^* = 610.92$ cal/mole, were determined by curve fitting the kinematic viscosity data obtained from Foley, Basak, and Delorey to the following equations taken from Eyring's viscosity equation:

$$\nu = B \exp\left(\frac{\Delta H^*}{RT}\right)$$

and:

$$B = \frac{N_o h \exp\left(\frac{-\Delta S^*}{R}\right)}{N_1 M_1 + N_2 M_2}$$

where:

ν = kinematic viscosity, cm^2/sec

N_o = Avogardo's number, (6.02×10^{23}) molecules/mole

h = Planck's constant, (1.38×10^{-16}) erg/^oK

N_1, N_2 = atomic fraction of component 1 or 2

M_1, M_2 = molecular weight of component 1 or 2

ΔH^* = enthalpy of activation, cal/mole

ΔS^* = entropy of activation, cal/(mole-^oK)

R = ideal gas constant (1.98717), cal/mole-^oK

T = temperature ^oK

Foley and Liu have reported self-diffusion data for thallium amalgams (9). They report data at 298^oK for compositions of .75, 7.13, 16.10, 20.04, 28.56, 34.60, 38.68, and 41.58 atomic percent thallium. Interpolation of their results to 1.414 atomic percent (1.440 weight percent) thallium, yields a diffusion coefficient of $.98 \times 10^{-5} cm^2/sec$. Extrapolation of the data presented in this work to 298^oK yields a value of 2.05×10^{-5}cm/sec. This indicates that the data from this work are approximately 100% higher than the value obtained from Foley and Liu. They used the capillary-reservoir technique

with a capillary diameter of 1 mm, while the capillary diameters used in this work were approximately 1.5 mm in diameter. Edwards, et al., (10) concluded that even under favorable conditions, convection effects will be appreciable for experiments conducted with capillary diameters greater than a few mm. However, wall effects could be more pronounced with the smaller diameter capillaries and thus have strong influence on the diffusion coefficient. The optimum capillary diameter,however, was not investigated in this work.

The major problem encountered in this research was the formation of gas bubbles in the capillaries. This prevented the capillaries from being completely full and caused the diffusion thread to be broken on one side of the capillary. Any runs in which the capillaries were not completely filled were discarded. Vacuum degassing at elevated temperatures for several hours was tried in an attempt to alleviate this problem. Use of this method showed a good deal of improvement in the results. However, it met with only limited success for runs made at $429^{o}K$, as indicated from the data scatter at this temperature.

Another problem encountered was slight variations in the count rate which produced large variations in the diffusion coefficient. This problem was lessened by taking large numbers of counts, usually 1 million, to reduce the random counting error. The errors in the self-diffusion coefficients, resulting from counting error are shown in Table 1.

Mercury-Zinc

Self-diffusion coefficients for the zinc amalgams percent zinc were measured by the modified shear-cell technique at 323, 373, 423, and 473^{o}K and are presented in Table III.

The data were fitted to the Arrhenius equation:

$$D - D_o e^{-E/RT}$$

where:

D = self-diffusion coefficient, cm^2/sec

R = gas constant, 1.98717 cal/gm-mole ^{o}K

T = temperature, ^{o}K

D_o = prexponential factor, cm^2/sec

E = activation energy, cal/gm-mole

The self-diffusion coefficients are plotted in Figure 2. The solid straight line represents the Arrhenius equation with the parameters $D_o = 4.6 \times 10^{-4}$ cm^2/sec and E = 1920 cal/gm-mole.

Using the self-diffusion coefficients of mercury in zinc amalgams published by Schadler and Grace (11) and the self-diffusion coefficients of zinc in zinc amalgams found in this study, the inter-diffusion coefficients of the system were calculated from Darken's equation (12).

Self-diffusion coefficients for 1.440 weight percent zinc in the zinc amalgam are compared to the data of Schadler and Grace (11) in Figure 2. The data of Schadler and Grace were interpolated to obtain values at 1.440 weight percent. Schadler and Grace presented data at 0.103, 0.488, and 1.630 weight percent over the temperature range 285^{o}K to 333^{o}K. They reported a standard deviation of 0.16×10^{-5} cm^2/sec for the 68 determinations at 0.488 weight

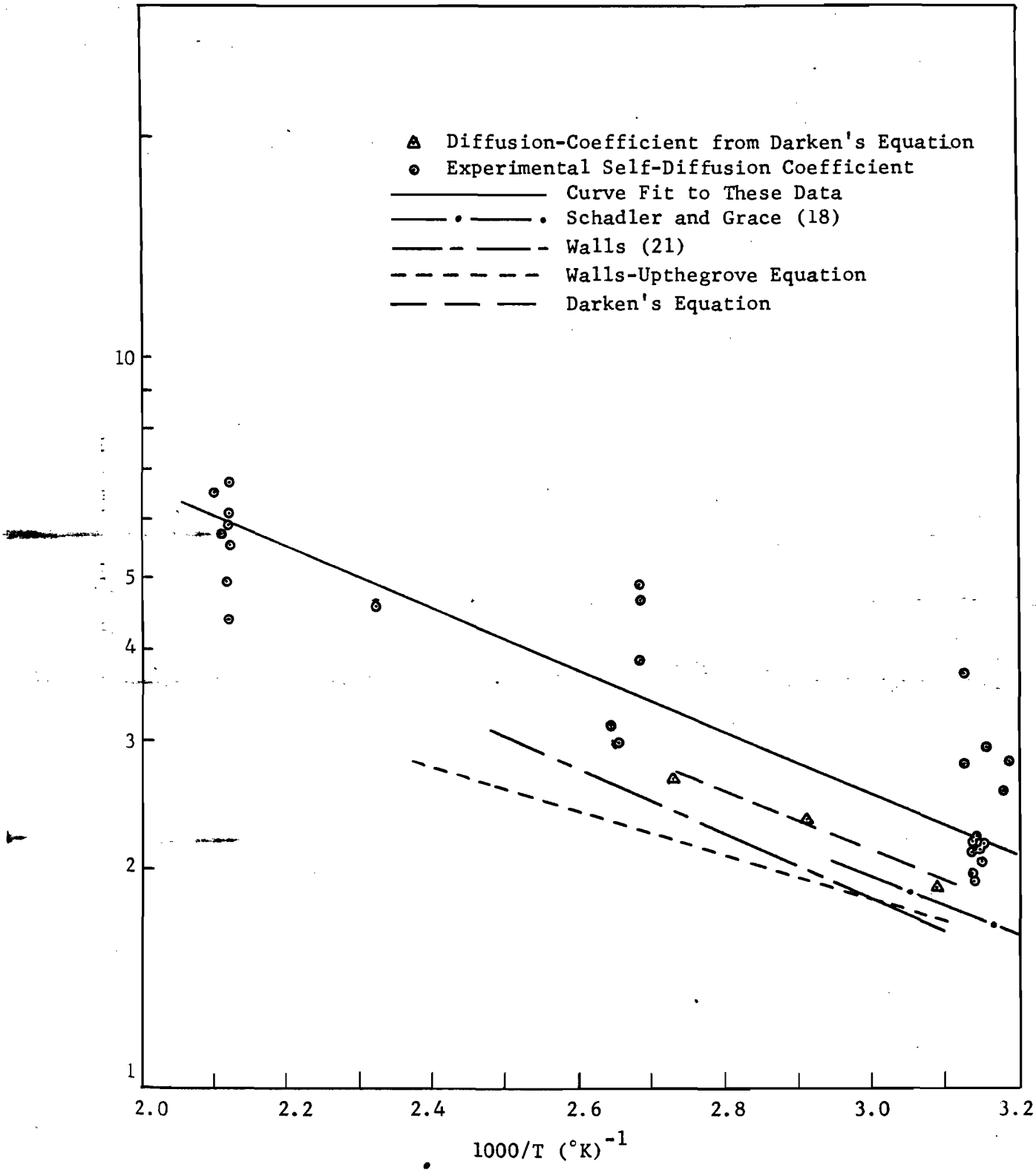

Figure 2. Self-Diffusion and Inter-Diffusion in 1.440 Weight Percent Zinc Amalgams.

TABLE III

MEASURED SELF-DIFFUSION COEFFICIENTS IN ZINC AMALGAMS AT 1.440 WEIGHT PERCENT

Temp (^oK)	$D \times 10^5$ (cm^2/sec)	Time (sec)	$\pm\Delta D \times 10^5$ (cm^2/sec)
318.2	1.91	32390	.02
318.2	1.94	39540	.01
317.2	2.01	46449	.02
318.2	2.11	36937	.02
318.2	2.11	36278	.03
317.7	2.16	33975	.03
318.7	2.17	38651	.03
318.2	2.18	47831	.02
314.1	2.54	31703	.02
319.8	2.75	56083	.03
313.3	2.72	41024	.03
316.2	2.91	30355	.02
319.6	3.67	50552	.02
377.2	2.98	33050	.03
379.2	3.12	62759	.02
373.2	3.83	31170	.04
373.2	4.66	30878	.05
373.2	4.83	60833	.03
431.2	4.52	29760	.04
472.2	4.37	45157	.03
472.2	4.88	36919	.03
468.2	5.51	31123	.04
473.2	5.62	38600	.04
471.2	5.89	49502	.04
472.2	6.03	47455	.04
477.2	6.54	29852	.04
471.2	6.76	45167	.04

percent and a standard deviation of 0.13 x 10^{-5} cm^2/sec for the 52 values of the self-diffusion coefficient at 1.630 weight percent. The self-diffusion coefficients determined in this work are about 30 percent higher than the self-diffusion coefficients measured by Schadler and Grace, but the slopes of the two curve fit lines are in good agreement. However, the pure mercury data of Schadler and Grace is about 30 percent lower than the majority of the reported pure mercury self-diffusion coefficients, including those determined by Broome and Walls (1) who used the modified shear-cell method. The standard deviation for the self-diffusion coefficients in this work is 0.69 x 10^{-5} cm^2/sec.

Walls' (8) data which covered a temperature range from 323°K to 393°K are also plotted in Figure 2. The composition of the amalgam in this work was 4.29 atomic percent zinc. The line shown on Figure 2 was obtained by extrapolating between 3.473 and 5.609 atomic percent zinc amalgam as given by Walls. A curve fit of Walls' data was not made and a standard deviation was not reported.

The inter-diffusion coefficients were calculated using activity coefficients obtained from Walls and Upthegrove (13) at the temperatures 323, 343, and 366°K. The self-diffusion coefficients for zinc were obtained from this work and the self-diffusion coefficients of mercury in zinc amalgams were obtained from the data of Schadler and Grace. The inter-diffusion coefficients of the system determined from the Darken equation are plotted in Figure 2.

PUBLICATIONS

A diffusion equation has been developed along the lines of a modified small fluctuation theory. The results were published in Metallurgical Transactions B. Two copies of the paper are enclosed.

PERSONNEL

The personnel involved in the experimental portion of the research were David W. Arnold and John E. Popielarczyk. Although neither of the above was supported by the grant, both completed Master of Chemical Engineering degrees. The titles of their research topics with an abstract of the work is enclosed.

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SELF-DIFFUSION PHENOMENA IN THALLIUM AMALGAMS

by

John Edmund Popielarczyk, Jr.

ABSTRACT

Self-diffusion coefficients for 1.440 weight percent thallium amalgams were measured at 303°K, 323°K, 376°K, and 429°K and atmospheric pressure using the modified shear-cell technique developed by Broome and Walls. These values are in fair agreement with the values predicted by the Walls-Upthegrove Equation. The data were fitted to an Arrhenius type equation giving:

$$D = 5.58 \times 10^{-4} \exp(-1961.19/RT)$$

where D is in cm^2/sec.

SELF-DIFFUSION PHENOMENA IN ZINC AMALGAMS

by

David Whisenant Arnold

ABSTRACT

Self-diffusion coefficients for 1.440 weight percent zinc amalgams were measured at 323, 373, 423, and 473^{o}K and atmospheric pressure using the modified shear-cell technique developed by Broome and Walls. These values are in fair agreement with the values determined by Schadler and Grace and by Walls who used the capillary-reservoir technique. The data were fitted to an Arrhenius type equation giving:

$$D = 4.6 \times 10^{-4} \exp(-1920/RT)$$

where D is in cm^2/sec.

The inter-diffusion coefficient for the system was calculated from the Darken equation and the self-diffusion coefficient from the Walls-Upthegrove Equation.